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PROCESS FOR MAINTAINING THE COMPOSITION OF VISCOSE PRECIPITATING BATHS CONTAINING MAGNESIUM SULPHATE

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In the manufacture of artificial threads, films, small bands and hairs from viscose, sulphuric acid precipitating baths are used, which, in addition to sodium sulphate, also contain magnesium sulphate. During use the amount of sulphuric acid contained in the spinning bath becomes reduced, owing to its being neutralized by the alkali of the viscose, and the quantity of the spinning bath decreases, because a portion of the liquid is carried away by the products, e. g., the threads, and passes into the washing water. The amount of sodium sulphate contained in the bath is, to a certain extent, automatically supplemented inasmuch as this salt is formed continuously by the double decomposition of the alkali with the sulphuric acid. Finally, gradual dilution of the spinning bath takes place, according to the amount of water contained in the viscose, and in the case of viscoses which are not very highly concentrated, not only compensates the loss of volume in the bath, due to the liquid being carried off by the thread, but may even cause the bath to increase in bulk. All these progressive changes which take place in the bath during the process of precipitating the viscose must be compensated or reversed, preferably at intervals but also progressively. Hitherto this has generally been effected by allowing any excess of the bath that may form to run away and making up the necessary concentration in sulphuric acid and salts by the addition of these substances to the bath from outside. In spinning baths of a simple kind, which contain only sulphuric acid and sodium sulphate as ingredients, it has repeatedly been proposed to employ so-called acid and salt regenerating processes, consisting in evaporating the diluted spinning baths, so as to counteract dilution by the water, or in evaporating the so-called upper baths, or the washing baths or subsequent fixing baths containing the same two substances and returning the concentrated product to the main spinning bath. When using such regenerating processes smaller quantities of fresh sulphuric acid and fresh sodium sulphate are required to make up the spinning bath to proper strength or such additions of fresh acid and

salt may, in some cases be entirely superfluous.

The present invention has for its object the provision and elaboration of a regeneration process which can be used for spinning baths which are required to contain magnesium sulphate in addition to sulphuric acid or sulphuric acid and sodium sulphate. That with such baths the simple evaporating process does not achieve the desired object has been shown by experiments, both with the main bath and also with the so-called upper baths, washing baths and the like. It has been found, as a matter of fact, that in the simple evaporation of bath solutions containing both salts simultaneously, the sodium sulphate content increases, disproportionately to the magnesium sulphate content, since fresh sodium sulphate is continuously being formed in the spinning bath. The result is that an excess of sodium sulphate is obtained while it is utterly impossible to keep the magnesium sulphate in solution in the manner required or to recover it. If the regeneration, particularly of the magnesium sulphate, is to be an effective and practical one and the above described composition of the main bath is to be obtained, it is necessary that a portion of the sodium sulphate be continuously removed.

Experiments have shown that if an attempt be made to free the bath solutions indicated from excess of sodium sulphate by crystallizing it out, the resulting deposits of salt generally contain magnesium sulphate in addition to the removed sodium sulphate and thus a proportion of magnesium sulphate is lost with the excess sodium sulphate.

A practical solution to these difficulties has now been provided in the way hereinafter described and this new method will first be described with reference to examples.

First example

Given a bath solution containing 130 gr. H_2SO_4 per litre, 190 gr. $MgSO_4$ per litre, 130 gr. Na_2SO_4 per litre.

The problem consists in freeing the bath mixture as completely as possible from so-

dium sulphate and then returning it in a concentrated form to the main spinning bath.

If any attempt be made to bring this bath solution into a condition for crystallizing out, by the usual methods of evaporation or cooling down, the desired end will not be achieved, because, in such case, a mixture of sodium sulphate and magnesium sulphate will precipitate.

The following method of procedure has, however, been found to be effective:

To the above mentioned bath is added 50 gr. per litre of magnesium sulphate, for instance, in the form of Epsom salts. After solution has taken place the bath is cooled down to a temperature of 8 to 10 deg. C. while stirring. In this case about 75 gr. of magnesium sulphate per litre separate out, as Epsom salt crystals, which are practically free from sodium sulphate. The separated mother liquor is now diluted by about from 5 to 10 per cent of its volume and the solution cooled down while stirring, to about -5 deg. C. During this cooling down sodium sulphate, practically free from magnesium sulphate, separates out in the form of Glauber salts and to the extent of more than 80 gr. of sodium sulphate per litre, so that, after the separation of the crystals, a final liquor remains which, as compared with the original bath solution present still contains 95% of H_2SO_4 , 84% of $MgSO_4$ but only 37% of Na_2SO_4 .

The remaining final liquor is now concentrated in a suitable concentrating apparatus and returned to the main spinning bath in the concentrated form together with the Epsom salts obtained in the first cooling down process and containing some sulphuric acid, for the purpose of revivification.

In this regeneration process in all 98% of H_2SO_4 and 97% of $MgSO_4$ are recovered but 63% of Na_2SO_4 separated out.

Second example

The bath is of the same composition as in the Example 1. This time the bath solution is first diluted by about 12% so that a bath with about 115 gr. H_2SO_4 per litre, 165 gr. $MgSO_4$ per litre, 115 gr. Na_2SO_4 per litre is obtained. This solution is now cooled down to about -5 deg. C. At this temperature sodium sulphate free from magnesium sulphate separates out in the form of Glauber salts and in such quantity that only about 47% of sodium sulphate per litre still remains dissolved. The remaining liquor is worked up and used as in Example 1. About the same degree of efficiency is obtained.

Third example

The bath solution to be operated on is composed of 130 gr. H_2SO_4 per litre, 240 gr. $MgSO_4$ per litre, 130 gr. Na_2SO_4 per litre.

This solution when cooled down to about 8 to 10 deg. C. is capable, without further

treatment, of separating out magnesium sulphate, free from sodium sulphate, in the form of Epsom salts. At this temperature 75 gr. of magnesium sulphate per litre separate out and a liquor is left which contains: 133 gr. H_2SO_4 per litre, 174 gr. $MgSO_4$ per litre, 132 gr. Na_2SO_4 per litre, a contraction in the volume of the bath by about 5% taking place at the same time, due to the water of crystallization removed with the Epsom salts. The filtrate is now diluted by 5 to 10% and then cooled down to -5 deg. C. At this temperature sodium sulphate free from magnesium sulphate separates out in the form of Glauber salts, that only about 50 gr. sodium sulphate per litre still remain in the residual liquor. The concentrated final liquor, poor in sodium sulphate, is used, together with the separated Epsom salts, for the revivification of the main spinning bath.

Fourth example

If the bath be composed of 120 gr. H_2SO_4 per litre, 160 gr. $MgSO_4$ per litre, 140 gr. Na_2SO_4 per litre, this solution may be cooled down to -5 deg. C. at once without dilution. Sodium sulphate free from magnesium sulphate separates out and the concentrated solution, poor in sodium sulphate, is again returned to the main spinning bath.

Fifth example

Let it be assumed that the bath solution to be worked up is composed of 100 gr. H_2SO_4 per litre, 200 gr. $MgSO_4$ per litre, 200 gr. Na_2SO_4 per litre. This bath may, like the one in Example 1, be worked up in two different ways:

(a) 40 gr. per litre magnesium sulphate are added to the bath. After solution has taken place it is cooled down but this time only to a temperature of 10 to 12 deg. C. At this temperature, notwithstanding the large amount of sodium sulphate contained in the solution, Epsom salts practically free from sodium sulphate is precipitated. If this temperature be exceeded a useless mixture containing a large amount of sodium sulphate results. The filtered off solution is then diluted by 5 to 10%, cooled to -5 deg. C. the Glauber salts separated out and the filtrate concentrated and returned, together with the previously separated Epsom salts, to the main bath.

(b) The solution to be treated is diluted by 15 to 20%, and then at once cooled down to -5 deg. C., so as to separate out Glauber salts, freed from crystals, evaporated and allowed to run back into the main spinning bath.

In the above examples the proportions and the procedure to be followed do not vary materially, even though the sulphuric acid content is subjected to considerable fluctuations (increasing, for example, to 150 gr. sulphuric

acid per litre and more or decreasing to 65 gr. per litre or less). In most cases, however, the sulphuric acid content in the ordinary spinning baths, upper baths and the like fluctuates within these limits.

The examples clearly show that the magnesium salt content per litre of bath to be treated is essentially the deciding factor as to the procedure to be adopted.

If the magnesium sulphate content does not amount to more than about 170 gr. per litre, separation of the Glauber salts may be effected at once by simple cooling.

If the magnesium sulphate content amounts to more than about 220 gr. per litre a portion of the magnesium sulphate may be separated out by a first cooling down to about 8 to 10 deg. C. and then, after suitable dilution, the main portion of the sodium sulphate can be caused to crystallize out by a further cooling down to -5 deg. C., for example.

If the magnesium sulphate content lies in the intermediate region between 170 and 220 gr. per litre, the magnesium sulphate content must first be increased by addition. Then the procedure may be as above described. Instead the magnesium sulphate content may be diminished to less than 170 gr. per litre, by suitable dilution, and then according to the first directions, the separation of the Glauber salts may be begun at once.

If, when the magnesium content is high, the amount of sodium sulphate contained is also large (see Example 5) the first cooling down when separating out the Epsom salts, must not be carried too far (say only to 12 deg. instead of to 8 to 10 deg.) as otherwise sodium sulphate would be precipitated in considerable quantity.

In an exactly similar manner, the cooling down must be kept within moderate limits when separating out the Glauber salts. If temperatures of -10 deg. C. and less be reached when the Glauber salts are being separated, there is risk of magnesium sulphate crystallizing out also if the amount thereof contained in the solution is considerable. In most cases it is well to be content to cool down to -5 deg. C.

The new process can be used partly for concentrating the main spinning bath and to free it from an excess of sodium sulphate. It can also be used for the working up of so-called drop baths which drop from spools or rollers, or of centrifuge baths which are slung off from spinning centrifuges, or of upper baths wherein spun spools are subsequently fixed or leached out. In any case the baths to be treated or parts thereof are advantageously worked up according to the process and the concentrated final liquor, poor in sodium sulphate, used with any Epsom salts otherwise separated for the revivification of the main spinning bath.

It must be appreciated that the terms "sodium sulphate" and "magnesium sulphate" respectively, used in the above specification and the claims will also comprise of course the aqueous crystalline precipitations, that is to say "Epsom salt" and "Glauber's salt."

What we claim is:

1. For maintaining the composition of sulphuric acid viscose precipitating baths containing magnesium sulphate and sodium sulphate in solution, a process comprising the following steps: crystallizing out at a magnesium sulphate content of more than 220 gr. per litre part of the magnesium sulphate in practically pure form by cooling, separating out the crystalline masses, diluting the resulting liquor and separating out sodium sulphate in practically pure form by further lowering the temperature, concentrating the resulting mother liquor and adding it with a proportion of magnesium sulphate to the precipitating bath to be revived.

2. For maintaining the composition of viscose precipitating baths containing in solution in addition to sodium sulphate, not less than 220 gr. per litre of magnesium sulphate, the process consisting in cooling down the bath solution to a temperature within the limits 8-10 deg. C. separating the mother liquor from the magnesium sulphate crystals thus formed, diluting the separated mother liquor by an amount within the limits 6-10%, cooling to approximately -10 deg. C. separating the resulting liquor from the sodium sulphate crystals thus formed, concentrating said resulting liquor and adding it with a suitable proportion of previously separated magnesium sulphate to the precipitating bath to be revived.

3. For maintaining the composition of viscose precipitating baths containing, in addition to sodium sulphate, a proportion of magnesium sulphate between the limits of 170 and 220 gr. per litre, the process consisting in augmenting the magnesium sulphate content to more than 220 gr. per litre, cooling the bath solution to a temperature within the limits 8-10 deg. C. separating the mother liquor from the magnesium sulphate crystals thus formed, diluting the separated mother liquor by an amount within the limits 6-10%, cooling to approximately -10 deg. C. separating the resulting liquor from the sodium sulphate crystals thus formed, concentrating said resulting liquor and adding it with a suitable proportion of previously separated magnesium sulphate to the precipitating bath to be revived.

In testimony that we claim the foregoing as our invention, we have signed our names.

JOHANN JOSEF STÖCKLY.
RICHARD BARTUNEK.

CERTIFICATE OF CORRECTION.

Patent No. 1,793,649.

Granted February 24, 1931, to

JOHANN JOSEF STOCKLY ET AL.

It is hereby certified that the name of the assignee in the above numbered patent was erroneously written and printed as "Vereinigte Glanzstoff-Fabriken A.-G.", whereas said name should have been written and printed as Vereinigte Glanzstoff-Fabriken A.-G., as shown by the records of assignments in this office.

Page 3, line 107, claim 3, for the misspelled syllable "diton" read dition; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of April, A. D. 1931.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.